MAGNETIC STUDIES OF SINGLE CRYSTALS CONTAINING TETRAHEDRALLY CO-ORDINATED Cu^{2+}, Ni^{2+} AND Co^{2+} IONS BETWEEN 300°K AND 90°K

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ABSTRACT. The paper reports the measurements on the single crystals of the salts of tetrahedrally co-ordinated Cu^{2+}, Ni^{2+} and Co^{2+} ions in $CuCs_2Cl_4$, $[(C_2H_5)_4]_2$ $NiBr_4$ and $CoCs_3$ Cl_5 respectively between 300°K and 90°K. The improved methods of measurements of magnetic anisotropy and mean susceptibility have been described in short. The results have been explained on the basis of refined ligand field theories of these ions developed recently by Bose *et al* (1965), taking the help of the optical and paramagnetic resonance studies. It has been shown that the experimental results can not be fully explained on the basis of the inversion of Stark pattern alone but have to be considered against the background of present refined theories which take into consideration the configurational interaction, overlap of the ligand and metal charge clouds and the variation of the crystalline electric field with temperature.

INTRODUCTION

Magnetic anisotropy and susceptibility of octahedrally co-ordinated ionic complexes of iron group of salts have been very extensively studied in our laboratory and elsewhere (Krishnan *et al* 1936, 1938, Mookherji, 1945, Bose, 1947, 1948; Guha, 1951, Jackson, 1927) to elucidate the various aspects of crystalline electric field theory. But very little work seems to have been done on the tetrahedrally co-ordinated salts (except $CoCs_2Cl_4$ and $CoCs_3Cl_5$, Krishnan and Mookherji, 1938; Bose, 1948) although their studies are sure to prove equally instructive. In the recent years a large number of such salts of Cu^{2+}, Ni^{2+} and Co^{2+} ions has been prepared and studied by X-ray and other physico-chemical methods.

It is well known that in the similarly co-ordinated salts of the transition group the cubic ligand field Stark patterns for the ions with d^n and d^{5+n} configurations are inverted with respect to the reciprocally related ions with d^{5-n} and d^{10-n} configurations (Van Vleck, 1932; Gorter, 1932). The same kind of inversion again takes place from an octahedrally to a tetrahedrally co-ordinated salt of the same ion, and in the latter case the overall cubic susceptibility and anisotropy behaviours of the tetrahedrally co-ordinated salts may be very different from the octahedral salts of the same ion and resemble to some extent the octahedral salts

of the reciprocally related ions. A study of these properties, especially of the anisotropy and its variation with temperature provides very sensitive indications of the details of such behaviours and throws more light upon their causes.

In view of the above, we have undertaken detailed experimental investigation of the magnetic anisotropy and susceptibility of three tetrahedrally co-ordinated complexes of Cu^{2+}, Ni^{2+} and Co^{2+} in the single crystals $CuCs_2Cl_4$, $[(C_2H_5)_4N]_2[NiBr_4]$ and $CoCs_3Cl_5$ respectively, between 300°K and 90°K. The details of the methods of measurements have been published earlier (Bose *et al*, 1963; Dutta Roy 1958). So only a summary of the methods is given here. The details of processing the experimental data for fitting the recent theories of the anisotropic tetrahedrally co-ordinated ions (Bose *et al*, 1965) are given and the results of such fittings are discussed.

EXPERIMENTAL TECHNIQUES OF MAGNETIC MEASUREMENTS

(a) *Anisotropy*

The apparatus for measuring the magnetic anisotropy of single crystals of the salts, consists of a circular 10 cm. diameter vernier torsion head reading rotations accurately to 0.1°. The crystal specimen with any desired orientation at the center of homogeneous magnetic field, is attached with "Peligom" or pure shellac cement to the lower end of a thin pyrex glass rod about 12 cm length and 0.5 mm. diameter, which is in its turn is suspended from the torsion head with a fine quartz fibre of about the same length and 0.01 mm diamter. A hexagonal set of small mirrors is attached to the upper end of the glass rod showing above the cryostat chamber. The image of an illuminated scale from one or other of the mirrors can always be observed as the crystal is rotated and gives the orientation of the crystal in the field accurately. The crystal is mounted to the fibre system removed outside the cryostat, with a known plane or axis horizontal or vertical as the case may be, with the help of a two circle goniometer and then replaced in proper position inside the crystal, mounted between the poles of a strong electromagnet. The magnetic field required is about 1000–3000 oersteds, produced between the plane parallel rectangular pole pieces (10 cm. × 15 cm) of the electromagnet, energised by current (2 to 3 amps.) from a D.C. 220 volt 15 KW stabilized generator.

When the magnetic field is switched on, the crystal in general, tends to set with its maximum susceptibility direction in the horizontal plane along the field, and any torsion produced thereby in the fibre is released by turning the torsion head. In this position there is no cuple acting on the crystal and no rotation on switching on or off the magnetic field, as observed very accurately by the mirror and scale arrangement. With the magnetic field off, the torsion head is rotated to bring the crystal at 45° to the above 'zero couple position'. Now the crystal will experience the maximum couple due to the field. The position of the light spot on the scale and the reading of the torsion head is very carefully noted and

the magnetic field is switched on. The crystal is strongly deflected but is slowly broubht back to its original position by rotating the torsion head, as can be checked by the return of the light spot. If α be the angle in degrees through which the torsion head is rotated from 45° position of the crystal, C the torsion constant of the fibre, H the magnetic field, M and m the molecular weight and mass of the crystal respectively, then the $gm.$ molecular magnetic anisotropy $\Delta\chi$ in the horizontal plane of the crystal is given by

$$\Delta\chi = \frac{2\alpha MC}{180mH^2} \qquad \ldots (1)$$

The superiority of the above method (Dutta Roy, 1958) over that of Krishnan and Banerjee (1936) is quite obvious. The present one being a null method, the experimental conditions can be maintained constant with a much greater precision, and the large uncertain correction factor for small angles of rotation of the head (less than 300°), with small anisotropies of the crystals or large torsion constant of the fibres, in the earlier method is avoided.

The accurate determinations of H, C etc. have been dealt at length by Datta (1954) and Dutta Roy (1958). The field is further checked by a proton resonance meter recently built here (Ghosh *et al* 1964). Corrections for the shape anisotropies of crystals are made with the help of empirically obtained data by Majumdar (1962). Small crystals are accurately weighed upto 10^{-6} gms with a Mettler microbalance. Use of dust free and air-conditioned chambers and other standard procedures for crystal preparation, crystal identifications polarographic check and accurate suspension of the crystals with the help of a goniometer, etc., have been discussed in details by Datta (1954).

In the case of small paramagnetic anisotropies of crystals a diamagnetic anisotropy correction needs to be made to a sufficiently good approximation from the measurements of anisotropies of isomorphous diamagnetic crystals using the method followed by Krishnan *et al* (1936) in the crystalline anisotropies themselves, or at a later stage when ionic anisotropies have been calculated.

For anisotropy measurements at any desired low temperature in the range 300°K to 90°K, the automatic gas flow type cryostat of Bose (1947) was used.

(b) *Mean Susceptibility*

The mean susceptibility was measured with the help of a very sensitive Curie-balance but of robust construction (Bose *et al*, 1963). Vertical suspension of the balance beam being of moderately thick phosphor bronze strip, the deflectional sensitivity has to be increased several thousand times by using a balanced pair of photo-electric cells, connected across a galvanometer and actuated by extremely small differences of illumination on the cells by a light spot, reflected from a mirror attached at the centre of the horizontal balance beam. The sample is

suspended vertically from one arm of the beam with a torsionless silk fibre in the central part of a Sucksmith type inhomogeneous horizontal magnetic field, with a small gradient at right angles to the field in the same plane (Dutta Roy, 1955). In the central region, $H\frac{dH}{dx}$ is sensibly constant over about 1 cm^3 volume. The crystal can freely turn round to have its maximum susceptibility axis in the horisontal plane along the field, and at the same time move bodily along the gradient. The effect of anisotropy of shape upon the rotation is eliminated by cutting the crystal in a square or cylindrical shape about the vertical axis, where necessary. The translational force on the sample is balanced electrodynamically by the force exerted on a small current bearing coil of insulated copper wire, rigidly attached to the same arm of the beam, as the crystal, with a long thick glass rod and placed with the coil parallel to the field, close to the sample. In practice, the potential drop across a suitable series of standard resistances for the requisite current in the coil (usually a few milliamperes) is measured with a Leeds and Northrup potentiometer with an accuracy of 0.1%.

The sample is enclosed in a new type of liquid oxygen cryostat (Bose *et al*, 1963) in which any desired temperature between 400°K and 65°K may be kept automatically constant within 0.01°K by isolating the experimental chamber from the cooling refrigerant liquid, the experimental chamber being a mirrored glass Dewar jacket the degree of vacuum in which can be changed by an adjustable air leak in the continuous high vacuum pumping system. A small heater is incorporated within the chamber so as to accurately balance the small heat leakage across the vacuum interspace. The refrigerant liquid is itself kept in a wide mouthed narrow tailed Dewar in which the experimental chamber is inserted. A constant volume air thermometer inserted in the experimental chamber and connected with a mercury contact magnetic relay operates the heater automatically.

The mass susceptibility of the sample at room temperature is calculated from the expression

$$\chi = \frac{e}{e_s}\left(\chi - \frac{k_s}{\rho_s}\right)\cdot\frac{m_s}{m} + \frac{k_a}{\rho} \qquad \ldots (2)$$

in which χ's are the mass susceptibilities of the samples along the field direction (mean value in case of powdered sample), e's the potential drops across a fixed resistance for the currents needed to balance the magnetic forces on the samples, corrected for the force upon the suspension system (including empty containers in the case of powders), m's their masses, ρ's densities; symbols with and without the subscript 's' refer to the standard (chromium potassium sulphate alum, Dutta Roy, 1955) and the unknown samples respectively; k_a is the volume susceptibility of surrounding air. Then knowing by comparison the susceptibility of the

unknown sample at a convenient reference temperature (say, 300°K), the susceptibility value at any other temperature (T) can be obtained by the relation

$$\chi_T = \chi \cdot \frac{e_T}{e_{300}} \left[1 - \frac{K_a}{K_{300}} (1 - \gamma \cdot 300)\left(1 - \frac{300}{T}\right)\right] \quad (3)$$

where K is the volume susceptibility of the crystal at 300°K, γ its volume coefficient of expansion. Suffixes T and 300 indicate values for the samples at T°K and 300°K respectively. The measurements have been taken at 15°, 10° or even closer temperature intervals when necessiated by a preliminary run to follow the temperature-susceptibility curve closely in a desired region. Since the room temperature in different seasons and times of the day will vary sometimes by more than 25°, it has been our practice to plot the value of e. T against T, giving a very nearly linear estra-or intrapolation near room temperatures to get the actual values at 300°K for both the standard and unknown samples. The values of χ_i at different temperatures are then calculated from the smoothed out values of e by graphical interpolation at short convenient intervals of temperatures.

A similar method of intrapolation is also adopted to get the values of anisotropy at the same set of temperatures from a graph of α T against T from measurements described in the previous section.

The gram molecular susceptibilities (χ_M) at any temperature are corrected for diamagnetism of the molecule and the square of the effective gram ionic moments (p_f^2) in Bohr magneton are calculated from

$$p_f^2 \quad \frac{3k}{N\beta^2} \quad \chi_M \cdot T = 7.995 \chi_M T^{*}. \quad (4)$$

N, β, k having the usual significances.

The notations for principal crystalline tensors are the usual ones used by magnetic workers. In the orthorhombic crystals the magnetic susceptibility axes coincide with the crystallographic axes and χ_a, χ_b, χ_c denote the susceptibilities along a, b, c axes corresponding to χ_i — 1, 2, 3 respectively. In the case of crystals with uniaxial symmetry (e.g. tetragonal, trigonal), $\chi_\parallel$ and $\chi_\perp$ denote the crystalline susceptibilities along and perpendicular to c, the crystalline symmetry axis, corresponding to $\perp$ = 1, 2, and $\parallel$ = 3. Ionic susceptibilities on the simplifying assumption that the ions have approximate uniaxial symmetry are given by $K_\parallel$ and $K_\perp$ along and perpendicular to the ionic symmetry axis corresponding to $\perp$ = x, y and $\parallel$ = z respectively. The method of calculation of $K_\parallel$ and $K_\perp$ using crystalline values are shown later

(c) *Preparation of the Crystals* :

The single crystals of $CuCs_2Cl_4$ were grown from an aquous solution of $CuCl_2$

* The values of the physical constants have been taken from Dumond and Cohen (1948).

and CsCl mixed in equimolecular proportions. The crystal generally grows in brownish orange colour in the form of elongated prisms along *b* axis.

Green tetraethylammonium nickel bromide crystals were prepared by slow evaporation of an equimolecular absolute alchohol solution of nickel bromide and tetraethylammonium bromide.

The deep blue crystals of $CoCs_3Cl_5$ were prepared from an aquous solution of $CoCl_2$ and CsCl in appropriate quantity at room temperature (about 30°C).

The reagents used were of the extra pure or guaranteed reagent quality of Merck or B.D.H.

STRUCTURAL DATA

(a) The structural analysis of $CuCs_2Cl_4$ by Helmholz and Kruh (1952) shows that the crystal belongs to the orthorhombic system (space group Pnma) with following parameters

$$a = 9.7 \text{ Å}$$
$$b = 7.6 \text{ Å}$$
$$c = 12.35 \text{ Å}$$

Each Cu^{2+} ion is at the centre of a tetrahedron formed by four Cl atoms at its vertices at an average distance of 2.22Å from the Cu^{2+} ion. The $[CuCl_4]^{2-}$ cluster is a tetragonal sphenoid having a four fold inversion symmetry about one of the line through central Cu^{2+} ion joining the middle points of two pairs of Cl atoms. This tetragonal symmetry axis is appreciably shorter in length than the other two such equal and mutually perpendicular bisectors lying in the plane normal to the said axis.

The unit cell of the crystal contains two pairs of the "magnetically inequivalent" $[CuCl_4]^{2-}$ clusters. From the detailed X-ray data on the various atoms in the unit cell, it is possible to calculate the direction cosines of the tetragonal axes of one pair of the $[CuCl_4]^{2-}$ clusters with respect to *a*, *b*, *c* axes of the crystals which are :

$$\alpha = 0.59307$$
$$\beta = 0$$
$$\gamma = 0.80543$$

The direction cosines of the tetragonal axes of the other pair of the $[CuCl_4]^{2-}$ cluster is same but with opposite signs. Since direction cosines occur as squares in the calculation of ionic susceptibilities, their signs do not matter. We shall need in the next section how these direction cosine values are utilized for the calculation of ionic susceptibilities.

(b) The X-ray studies by Peter Pauling (as quoted by Gill and Nyholm, 1959) of a series of isomorphous organometallic halides of Ni^{2+} like $[(C_2H_5)_4]_2NiBr_4$ indicate that the crystal belongs to the cubic system (space group $P2_1/3$)

with four molecules in the unit cell of dimension $a = 15.5$ Å. The X-ray results also show that the Ni^{2+} ion is tetrahedrally co-ordinated with four halogens forming a trigonally distorted tetrahedron round the Ni^{2+} ion. The trigonal axis passes through the halogen at one of the vertices of the tetrahedron and the central Ni^{2+} ion, and is normal to the base formed by other three halogens. Evidently, this trigonal axis is a body diagonal of the unit cell. But the detailed results of the structure are not known since the X-ray results of Peter Pauling do not appear to have been published. However, since the crystal is cubic we can only measure the mean susceptibility of the crystal and do not require X-ray data for correlation with the ionic mean susceptibility.

(c) The structural analysis of $CoCs_3Cl_5$ by Powell and Wells (1935) reveals that in this salt the Co^{2+} ion is tetrahedrally co-ordinated with four chlorine atoms at an average distance of 2.34 Å from the central Co^{2+} ion. The crystal belongs to the tetragonal system (space group D_{4h}^{16}) with four molecules in the unit cell of dimensions

$$a = 9.18\text{Å} \qquad c = 14.47\text{Å}$$

The tetrahedron is slightly distorted along one of the axes which is a four fold inversion axis and passes through the midpoints of two pairs of adjacent chlorine atoms and the central Co^{2+} ion. The tetragonal axes of the four molecules being all parallel to the 'c' axis of the crystal, the crystalline ellipsoid coincides with the molecular ellipsoid and hence no structural parameters are required to get the ionic susceptibilities.

CALCULATION OF IONIC SUSCEPTIBILITIES IN $CuCs_2Cl_4$

The ionic susceptibilities of $CuCs_2Cl_4$ have been calculated following the method of Ghosh and Mitra (1964). A short outline of the method is given below The direction cosines of the three principal ionic susceptibility tensors (K_1, K_2, K_3) with respect to an arbitrary orthogonal system (x, y, z) is given as

	x	y	z
K_1	α_1	β_1	γ_1
K_2	α_2	β_2	γ_2
K_3	α_3	β_3	γ_3

If χ_{max} and χ_{min} represent the maximum and minimum susceptibilities in a given horizontal section of the crystalline ellipsoid in which magnetic measurement is to be made, having Millerian indices (h, k, l), then for n inequivalent ions in the unit cell,.

$$\chi_{max} + \chi_{min} = K_1\left[1 - \frac{1}{n}\sum^{n}\{(\alpha_1^2\xi^2 + \beta_1^2\eta^2 + \gamma_1^2\zeta^2) + 2(\alpha_1\beta_1\xi\eta + \alpha_1\gamma_1\xi\zeta + \beta_1\gamma_1\zeta\eta)\}\right]$$

$$+ K_2\left[1 - \frac{1}{n}\sum^{n}\{(\alpha_2^2\xi^2 + \beta_2^2\eta^2 + \gamma_2^2\zeta^2) + 2(\alpha_2\beta_2\xi\eta + \alpha_2\gamma_2\xi\zeta + \beta_2\gamma_2\eta\zeta)\}\right]$$

$$+ K_3\left[1 - \frac{1}{n}\sum^{n}\{(\alpha_3^2\xi^2 + \beta_3^2\eta^2 + \gamma_3^2\zeta^2) + 2(\alpha_3\beta_3\xi\eta + \alpha_3\gamma_3\xi\zeta + \beta_3\gamma_3\eta\zeta)\}\right] \quad \ldots \quad (5)$$

where ξ, η, ζ are the direction cosines of the normal to the given (h, k, l) plane relative to $x, y,$ and z. And,

$$\chi = \frac{1}{3}(\chi_1 + \chi_2 + \chi_3) = \frac{1}{3}(K_1 + K_2 + K_3) = K$$

For $CuCs_2Cl_4$ which is an orthorhombic crystal with a uniaxial symmetry of the ion, x, y and z are taken to coincide with a, b and c axes of the crystal respectively, and

$$K_1 = K_2 = K_\perp \text{ and } K_3 = K_\parallel$$

Hence the equation (5) with 'b' axis vertizal (for magnetic in measurement to be made [010] plane) reduces to ($\eta = 1$, $\xi = \zeta = 0$)

$$\chi_c + \chi_a = K_\parallel(1 - \beta_3^2) + K_\perp(1 + \beta_3^2) \quad \ldots \quad (6)$$

$$\chi = \frac{K_\parallel + 2K_\perp}{3}$$

where β_3 is the direction cosine of the tetragonal axis of the ion with respect to 'b' axis obtained from X-ray measurement and is, as we calculated earlier, equal to zero. $(\chi_c + \chi_a)$ can be determined from two anisotropy and the mean susceptibility measurements by the methods described earlier $(K_\parallel \sim K_\perp)$ and K may be obtained from equation (6). The same equation also determines uniquely whether $(K_\parallel - K_\perp)$ is positive or negative. The data for the crystalline anisotropies and mean susceptibilities at different temperatures are given in the 2nd, 3rd and 4th columns of the table I and the ionic anisotropies are shown in column 7-th. In the absence of structural data at all temperatures, we have to assume that the direction cosine in equation (6) remains constant with temperature. Since the tetragonal axis of the Cu^{2+} ion lies in the (010) plane with $\beta = 0$, such an assumption is justified so long as this special symmetry is unchanged.

STARK PATTERNS AND INFORMATIONS ON THEM OBTAINED FROM OPTICAL ABSORPTION STUDIES OF TETRAHEDRALLY CO-ORDINATED COMPLEXES

From what has been said earlier about the inversion of the Stark pattern for tetrahedral complexes, the pattern under the predominant cubic part of the crystal field in such Cu^{2+} complexes will consist of an orbital doublet ^2E_g and a triplet ^2T_g with the triplet lying lowest. The superimposed tetragonal component of the field will break this triplet into a single Kramers spin doublet and a pair of coincident doublets, separated by Δ cm^{-1} where Δ is the anisotropic field splitting.

TABLE 1

$CuCs_2Cl_4$

Temp. K°	$(\chi_c-\chi_b)\times10^6$	$(\chi_c-\chi_a)\times10^6$	$\chi \times 10^6$	$K_{\parallel}\times10^6$	$K_{\perp}\times10^6$	$(K_{\parallel}-K_{\perp})\times10^6$
300	341	156	1680	2031	1505	526
290	351	161	1733	2094	1552	542
280	263	167	1790	2161	1604	557
270	374	173	1853	2237	1661	576
260	385	178	1918	2313	1720	593
250	398	184	1989	2401	1783	618
240	412	190	2068	2495	1854	641
230	425	196	2151	2594	1929	665
220	443	203	2244	2703	2015	688
210	461	210	2345	2817	2109	708
200	481	218	2420	2945	2211	734
190	501	226	2578	3085	2325	760
180	525	236	2713	3242	2445	797
170	549	247	2866	3417	2586	831
160	587	260	3037	3621	2745	876
150	607	275	3231	3845	2922	923
140	638	290	3452	3103	3127	976
130	674	308	3709	4100	3363	1037
120	715	330	4007	4748	3636	1112
110	769	352	4361	4818	3633	1185
100	811	376	4784	5628	4362	1266
90	869	401	5321	6220	4870	1350

TABLE II

$\vee[(C_2H_5)_4N]_2NiBr_4$

Temperature °K	$\chi_M \times 10^6$	$\mu_{\vee}^2$
300	5986	14 36
290	6193	14 34
280	6387	14 30
270	6601	14 26
260	6840	14 22
240	7348	14 10
230	7646	14 06
220	7959	14 00
210	8302	13.94
200	8674	13 87
190	9008	13 81
180	9536	13.72
170	10223	13.69
160	10639	13 61
150	11809	13.54
140	11909	13.33
130	12777	13.28
120	13696	13.28
110	14758	12.98
100	16010	12.80
90	17358	12.49

TABLE III

$CoCs_3Cl_5$

Temp °K	$(\gamma_\parallel - \gamma_\perp) \times 10^6$	$K_\delta \times 10^6$	$K_\parallel \times 10^6$	$K_\perp \times 10^6$	$(K_\parallel - K_\perp) \times 10^6$
300	652	9093	9528	8876	652
290	666	9407	9851	9185	666
280	689	9732	10192	9502	689
270	718	10083	10562	9844	718
260	750	10481	10981	10231	750
250	790	10875	11402	10612	790
240	833	11303	11858	11025	833
230	883	11752	12341	11458	883
220	937	12235	12860	11923	937
210	998	12704	13369	12371	998
200	1073	13300	14008	12935	1073
190	1154	13947	14716	13562	1154
180	1240	14634	15461	14221	1240
170	1338	15395	16322	14985	1338
160	1448	16268	17233	15785	1448
150	1561	17274	18328	16747	1581
140	1737	18453	19758	17841	1737
130	1907	19862	21133	19226	1907
120	2089	21421	22814	20725	2089
110	2337	23155	24713	22376	2337
100	2677	15176	26961	24284	2677
90	3245	27807	30002	26757	3345

The recent optical absorption studies of $CuCs_2Cl_4$ at 77°K by Ferguson (1964, see Fig. 1a) have revealed that this anisotropic field splitting is as high as 5000 cm^{-1} and is comparable in magnitude with the cubic field separation which is 9000 cm^{-1}. Such a high anisotropic field splitting appears to be rather rare amongst the iron group of salts. The polarised spectral studies of Lawson and Morrison (1961) also reveal such high magnitude of anisotropic field separation in this salt. It is also observed that the cubic field splitting is nearly 3/4 of 12300 cm^{-1}, that observed in octahedral Cu^{2+} complex in the hydrated halides (Dreich and Trommer, 1937) instead of 4/9 as expected from theory. As we shall presently see, there are enough indications to show that the magnetic behaviour of the Cu^{2+} ion in this case is quite different from what is to be expected from the inversion of Stark pattern alone. The magnetic behaviour depends sensitively upon whether the singlet or the doublet component of the triplet $^2T_2$ lies lowest in the Stark pattern and hence decides whether Δ will be positive or negative. The spin-orbit coupling in Cu^{2+} is the highest in the iron group and considerable admixtures the various levels will take place under its action.

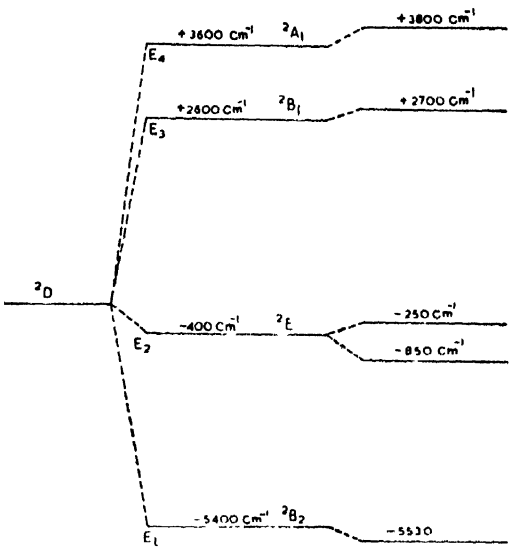

Fig. 1(a) Stark Pattern of Tetrahedrally Co-ordinated Cu^{2+} ion in $CuCs_2Cl_4$ (Ferguson, 1964). (Not to Scale).

In the case of the Ni^{2+} tetrahedral complex in the salt the predominant cubic ligand field breaks up the ^3F ground state of the free ion into two triplets $^3T_1$ and $3T_2$ and a singlet $^3A_2$ arranged in ascending order of energy. The samll superposed trigonal component of the field further splits up the lowest triplet $^3T_1$ into a doublet ($^2E_2$) and a singlet $^3A_1$, separated by Δ cm^{-1}, the anisotropic field splitting. Which of these two ($^2E_2$, $^3A_1$) will lie lowest, depends upon the sign of Δ and is to be decided from the experimental data. These levels will be further split up by the spin-orbit coupling which will mix up the different states and new states will be obtained. The Stark pattern of this complex is shown diagramatically in figure (1b). In the figure the ^3P level is also shown since this will give admixtural contributions to the ground state as also high frequency type contributions.

The optical absorption of an isomorphous tetrahedral Ni^{2+} salt in mull has been studied by Gill and Nyholm (1959) and Goodgame *et al* (1961) at room temperature. They have observed bands round about 12,000 cm^{-1} and 6900 cm^{-1}. The former is assigned to be due to the transition $^3T_1(F) \rightarrow {}^3T_1(P)$ and latter to $^3T_1(F) \rightarrow {}^3A_2$. This gives the cubic field coefficient (Dq) as nearly -380 cm^{-1}. The cubic field coefficient (Dq) for octahedrally co-ordinated $NiSiF_6 \cdot 6H_2O$ is nearly 1000 cm^{-1} (Pryce *et al*, 1964). It has been shown by Jorgenson (1956) that a reduction in Dq of $\sim 25\%$ occurs while going from water to halogen ligands with the same paramagnetic ion. This indicates that in the present case Dq of tetrahedral

Ni^{2+} ion is about 4/9th that of the octahedral one as expected from theory, after allowing for the reduction due to chlorine ligands.

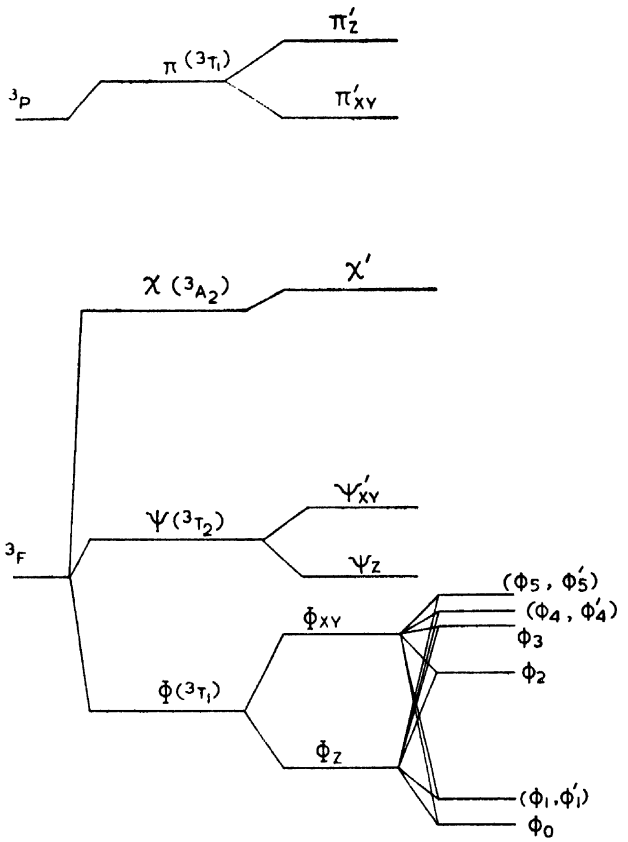

Fig 1(b) Energy Level Diagram for Ni^{2+}ion in Tetrahedral Co-ordination. (Not Drawn to Scale.)

The Stark pattern of the tetrahedral Co^{2+} ion in the cubic field will be similar to that of octahedral Ni^{2+} with an orbital singlet lying lowest. The ^4F ground state of free Co^{2+} ion is split up by the predominant cubic field of the ligand tetrahedron into an orbital singlet ($^4A_2$) and two triplets $^4T_2$ and $^4T_1$ arranged in ascending order of energy. In the superimposed tetragonal field, the above triplets break into a singlet fins a doublet to the extent of about 500 cm^{-1} (Bose *et al*, 1965c). With the spin-orbit interaction included, the lowest $^4A_2$ level splits up into two Kramers doublet with a separation of about 9 cm^{-1} (Hall and Hayes, 1960). The Stark pattern of the tetrahedral Co^{2+} ion is shown in figure (1c).

Cotton *et al*, (1961) have done extensive investigations of the spectra of $[CoCl_4]^{2-}$ complexes in different solution and mulls. In the spectra of $CoCs_3Cl_5$

in hexachlorobutane mull, which may be taken to represent the spectra of the salt itself, band are observed near 5580 cm^{-1} and 14000 cm^{-1} owing to the transitions

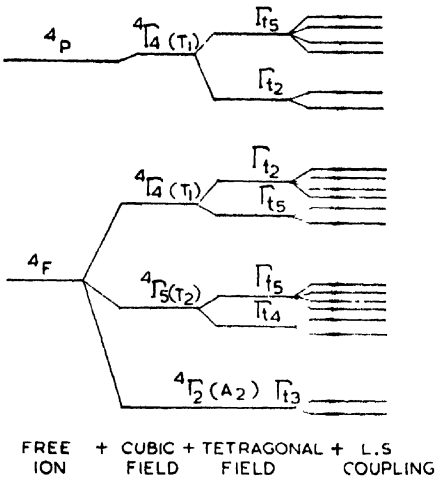

Fig. 1(c) Energy Level Diagram for Co^{2+} ion in Tetrahedrally Co-ordination.
(Not to Scale)

$^4A_2 \rightarrow {}^4T_1(F)$ and $^4A_2 \rightarrow {}^4T_1(P)$ respectively. They have also been able to resolve these bands into five and four components respectively. The value of Dq as found by Cotton *et al* (1961) is 325 cm^{-1}. It may be mentioned that the Dq for the octahedral hydrated Co^{2+} complexes (Pappalardo, 1954) is nearly 980 cm^{-1} which is about 9/4 times the former when we remember that a reduction of Dq by $\sim 25\%$ occurs while going from the water to halogen co-ordination (Jorgenson, 1956).

Since the cubic field separation in tetrahedral complex is less than half that of the octahedral co-ordination in the former case the effect of second order perturbation terms becomes relatively more important. Moreover, in the tetrahedral case the absence of a centre of symmetry may justify the retention of odd order harmonics in the expression for the ligand field potential. As a consequence configurational interaction between the 3d and 4p orbitals of the metal ion arises and modifies the 3*d* wavefunctions. The effect of configurational interaction is to modify the orbital overlap factors (κ) and spin-orbit coupling coefficient (ζ) in the crystal. Hence the reduction in κ and ζ in tetrahedral case is not only due to the scrambling of the metal and ligand orbitals as in the octahedral case, but also partly to the configurational interaction though according to Low (1960) and Weakliem (1962) this latter part appears to be rather small in comparison to the former. It is also important to note that such reductions are essentially anisotropic in character.

Recently the expressions for the magnetic anisotropy and susceptibility of these tetrahedrally co-ordinated complexes, of Cu^{2+}, Ni^{2+} and Co^{2+} have been

deduced in our laboratory taking into account the special features of the present case and fitted with the experimental values. The details of the theory are under publication (Bose *et al*, 1965a, 1965b, 1965c). In the present paper we give the theoretical expressions of the susceptibilities and describe the trial and error method of calculating the various physical parameters arising in the said theoretical expressions from the magnetic anisotropy and mean susceptibility data given in an earlier section, and checking them with spectroscopic and paramagnetic resonance data wherever available.

THEORETICAL EXPRESSIONS FOR THE IONIC SUSCEPTIBILITIES FOR THE TETRAHEDRALLY CO-ORDINATED Cu^{2+}, Ni^{2+} AND Co^{2+} COMPLEXES

(i) *Cu^{2+} ion*

The expressions for the ionic susceptibilities of the tetrahedrally co-ordinated Cu^{2+} ion in $CuCs_2Cl_4$ have been deduced by Bose *et al* (1965a) following Pryce's Spin Hamiltonian formalism (1950). The expressions are :

$$K_{\parallel} = \frac{8N\beta^2\kappa'^2_{\parallel}}{E_3 \quad E_1} + \frac{N\beta^2}{4\kappa} \cdot \frac{G_{\parallel}^2}{T}$$

$$K_{\perp} = 2N\beta^2\left[\frac{k_{\perp}^2}{E_2 \quad E_1} - \frac{\zeta R_{\perp} k_{\parallel}}{(E_2 \quad E_1)^2}\right] + \frac{N\beta^2}{4k} \cdot \frac{G_{\perp}^2}{T} \qquad \ldots (7)$$

where $K_{\parallel}$ and $K_{\perp}$ are the gram ionic susceptibilities along and perpendicular to the tetragonal axis. The explicit expressions for the different parametral symbols are given in the theoretical paper (Bose *et al*, 1965a). It can be mentioned here that E's are the energy values (shown in the Fig. 1a) which involve the cubic field parameter G and anisotropic field parameters H and I. Other physical parameters involved in the expression are the spectroscopic splitting factors $G_{\parallel}$, G in the crystal, orbital reduction factors ($\kappa_{\parallel}$, $\kappa_{\perp}$) and spin—orbit coupling reduction factors ($R_{\parallel}$, $R_{\perp}$), subscripts $\parallel$, $\perp$ refer to the quantities parallel and perpendicular to the tetragonal axis. The factor $R_{\parallel}$ in this expression does not enter in the 2nd order terms with the square brackets but is involved in the expression for $G_{\parallel}$.

(ii) *Ni^{2+} ion*

The expression of mean susceptibility which could only be measured in this case, has been deduced by Bose *et al* (1965b) on molecular orbital approximation. The expression is :

$$K = \frac{N\beta^2}{3k} B_1\left[\frac{2A^2}{T} + \frac{16B^2k}{D}\left\{\exp\left(\frac{D}{kT}\right) - 1\right\}\right]$$

$$+\frac{N\beta^2}{3}B_1\Bigg[\Bigg\{\frac{8(c+\frac{1}{2}\alpha' k_\perp d)^2}{E_2-E_1}+\frac{8\{bc-2ad+\frac{\alpha' k_\perp}{2}(2ac-bd)\}^2}{E_3-E_1}$$

$$+\frac{4c^2d^2(\alpha k_\parallel+2)^2}{E_4-E_1}+\frac{16(c-\frac{1}{2}\alpha' k_\perp d)^2}{E_5-E_1}\Bigg\}$$

$$+\Bigg\{\exp\left(\frac{D}{kT}\right)\left(\frac{4a^2(\alpha k_\parallel+2)^2}{E_2-E_0}+\frac{16\{(ad-bc)+\frac{\alpha' k_\perp}{2}(ac-bd)\}^2}{E_4-E_0}\right)\Bigg\}\Bigg] \quad (8)$$

The explicit expressions for the different parameteral symbols in the above expression is given in the theoretical paper (Bose *et al*, 1965b). It is seen from there that there are five physical parameters in this case (Δ, $P_\parallel$, $P_\perp$, $Q_\parallel$, $Q_\perp$) where Δ is the anisotropic field coefficient and $P_\parallel = \alpha R_\parallel \zeta$, $P_\perp = \alpha' R_\perp \zeta$, $Q_\parallel = \alpha k_\parallel$, $Q_\perp = \alpha' k_\perp$; α, α' being the Lande factors along and perpendicular to the symmetry axis of the ion. ζ is the free ion spin-orbit coupling coefficient and R_i ($i = \parallel$ or $\perp$) are the reduction factors associated with the matrix element for spin-orbit coupling. $\kappa_\parallel$, $\kappa_\perp$, $R_\parallel$, $R_\perp$ are as before the orbital reduction overlap factors and spin orbit coupling reduction factors parallel and perpendicular to trigonal axis.

(iii) Co^{2+} ion

The expressions for the ionic susceptibilities of the tetrahedrally co-ordinated Co^{2+} ion have been deduced by Bose *et al* (1965c)by spin Hamiltonian formalism. The expressions for $K_\parallel$ and $K_\perp$ are given below

$$K_\parallel = 8N\beta^2\alpha_\parallel k_\parallel\left\{\frac{15}{32}\frac{g_\parallel^2}{T}+\frac{3D}{8kT^2}\cdot g_\parallel^2\right.$$

$$K_\perp = 8N\beta^2\alpha_\perp k_\perp{}^2\left\{\frac{15}{32}\frac{g_\perp^2}{T}+\frac{3D}{16kT^2}\cdot g_\perp^2\right. \quad (9)$$

Here α's are the inverse of energy difference and envolve the usual field parameters, D_q, H and I. The other parameters envolved in the expressions already explained earlier are k_i and ζ_i ($i = \parallel$ and $\perp$). D is the 'Zero-field splitting' and g_i($i = \parallel$ and $\perp$) are the spectroscopic splitting factors. The detailed expressions are given in the theoretical paper (Bose *et al*, 1965c).

CALCULATION OF THE PHYSICAL PARAMETERS IN THE EXPRESSIONS FOR THE SUSCEPTIBILITIES FROM EXPERIMENTAL DATA

While fitting the experimental results already given with the theoretical expressions in the cases where an orbital singlet is lying lowest (i.e. in tetrahedral Co^{2+} and Cu^{2+}), we notice that there are seven adjustable parameters viz. D_q (or

G), H, I, $k_{\|}$, $k_{\perp}$, $\zeta_{\|}$ and $\zeta_{\perp}$. Theoretically all these parameters are independent; the relative values of $k_{\|}$ and $k_{\perp}$, $\zeta_{\|}$ and $\zeta_{\perp}$ dependent on the lower symmetric field parameters. H and I, although they may not be explicitly expressible in terms of them; so that there are, effectively, only five independent parameters. We can then decide uniquely the values of these parameters by fitting with the mean susceptibility data alone for at most seven (theoretically five) temperatures, if all these parameters are assumed to remain constant with temperature. In this particular case we have the anisotropy data as well. Hence a unique choice of the parameters is always possible with at most four pairs of anisotropy and mean susceptibility data at four temperatures provided the parameters do not vary with temperature. With this assumption holding strictly valid, these values of the parameters should be consistent not only with the mean susceptibility and anisotropy data at other temperatures but also with the paramagnetic resonance data and the fine structure optical absorption data.

In actual practice, owing to the complicated nature of the equations, we had to use a trial and error method to find the values of the parameters and it became immediately obvious that no single set of parameters could be consistent with all the available data. Hence the conclusion is that the given set of parameters obtained for magnetic data at the requisite number of temperatures can be a unique solution for data these only at the given temperatures, and for no other data; so that the set of parameters cannot have much physical significance, and hence the assumption that they are independent of temperature is not valid. Finally, we proceeded as follows to bring out properly the systematic discrepancy in fitting the data with the theory In the case of Co^{2+} it is seen that the optical fine structure data of Cotton *et al* (1961) are available only at room temperature whereas the paramagnetic resonance data of Bowers and Owen (1955) are for 90°K. Since the room temperature magnetic anisotropy and susceptibility data are always taken as standard and also the energy levels of the optical absorption are of primary importance in thecalculation of susceptibilities, we found out by extensive trial the set of values which gave practically exact fit with the experimental mean susceptibility and anisotropy data at room temperature, consistent with optical absorption data. These data are enough to give a qunique solution of the parameters at room temperature only and will have a physical reality for this temperature. In the case of Cu^{2+}, since the g-values (Sharnoff, 1964) and fine structure optical absorption data of Ferguson (1964) are available at 77°K and are not supposed to change appreciably at 90°K, the lowest temperature of our magnetic measurements, we found out as above the set of parameters which gave practically exact fit with experimental susceptibility and anisotropy at this temperature, consistent with the paramagnetic resonance and optical absorption data. If these sets of parameters for Co^{2+} and Cu^{2+} had been constant with temperature, then it could be expected that they would give good fit with the magnetic data at all other temperatures.

But in both cases systematic deviations are found to occur which is especially prominent in anisotropy. While fitting the experimenal data in the case of Ni^{2+} with the expression of mean susceptibility (eq^n.8), we notice that there are five adjustable parameters (Δ, $P_{\|}$,$P_{\perp}$, $Q_{\|}$, $Q_{\perp}$) whose values can be uniquely decided by fiitting with the mean susceptibility data at five temperatures (theoretically three since the relative magnitudes of $P_{\|}$, $P_{\perp}$ and $Q_{\|}$, $Q_{\perp}$ afe dependant on Δ), if the parameters are assumed to remain constant with temperature. However, in view of the large number of earlier experimental findings (Bose *et al*, 1960. 1961$_a$, 1961*b*, 1964), it is very unlikely that the anisotropic field coefficient Δ should remain constant with temperature even if the others are assumed to be so a first approximation. But since we do not have any anisotropy or resonance data, we are not able to find the values of Δ at diffrent temperatures from mean susceptibility alone, which could only be measured for this cubic crystal. On attempting to fit the experimental values on mean susceptibility, it is found that no single set of the above parameters can bring the fitting within the limits of experimental error at all temperatures When the closest approach to one values at a given temperature is made with a given set of parameters, the values at other temperatures show systematic increasing differences Since the room temperature experimental mean moment is always treated as standard, we found out tqe set of values of the parameters which gave a very close approach to it within the limits of experimental errors with the calculated mean value. The causes of these discrepancies will be discussed in due course.

DISCUSSIONS

(a) *Cu^{2+}* ion

(i) *Room Temperature Mean Moment and Magentic Anisotropy*

As we have seen earlier, the magnetic behaviour of tetrahedrally co-ordinated Cu^{2+} ion ($3d^9$) should be somewhat similar to the octahedrally co-ordinated Fe^{2+} ($3d^4$) or Ti^{3+}($3d^1$) if all other considerations are identical. The mean moment of Cu^{2+} ion in $CuCs_2Cl_4$ is 2 02 (Table I) whereas for octahedral Cu^{2+} in $Cu(NH_4SO_4)_2.6H_2O$ it is 1.95 (Bose, 1948), both values being at 300°K. The spin only value for the ^2D state of Cu^{2+} ion is 1.73. Thus the orbital contributions in the case of tetrahedral and octahedral Cu^{2+} are about 16 and 13 percents respectively. The mean magnetic moment of octahedral Fe^{2+} ion in $Fe(NH_4SO_4)_2.6H_2O$ at 300°K is 5.66 (Bose, 1948) as against the spin only value of 4.89, thus showing an orbital contribution of the order 17 percent. It should be remembered that although the Stark pattern in both the tetrahedral Cu^{2+} and octahedral Fe^{2+} should be similar with a triplet lying lowest, the actual magnetic behaviour in $CuCs_2Cl_4$ is rather different owing to three reasons. Firstly the spin-orbit coupling in Cu^{2+} is about eight times that in Fe^{2+}, giving more admixture with upper levels. Secondly, the spin contribution to the moment is about 3 times larger in Fe^{2+} making the percentage orbital contribution appear smaller. Thirdly, as has been mentioned

earlier the optical absorption spectra of $CuCs_2Cl_4$ show that under the action of the total ligand field the lowest orbital singlet with two fold Kramers spin degeneracy is separated from the next higher level by 5000 cm^{-1}. On the other hand the axial field separation of the lowest cubic triplet in octahedral Fe^{2+} is only 600 cm^{-1} (Bose *et al*, 1961). Thus although the spin-orbit coupling in tetrahedral Cu^{2+} is nearly eight times the octahedral Fe^{2+}, and the cubic field separation being comparable (the cubic field separation in octahedral Fe^{2+} is about 10300 cm^{-1}; Dreisch and Kallschener, 1944), the orbital contributions are nearly equal. In the octahedral Cu^{2+}, the cubic field spearation is about 12000 cm^{-1} and the tetragonal separation of the lower 'non-magnetic' orbital doublet is about 1000 cm^{-1}. Orbital contribution thus comes only from the upper orbital triplet through spin-orbit coupling. It is then difficult to understand why the orbital contributions are apparently about the same in the two cases, unless it is assumed that a strong covalency effect reduces the normally expected orbital contributions in the tetrahedral case. Again though octahedral Ti^{3+} ion is very similar to tetrahedral Cu^{2+} in respect of orbital as well as spin degeneracy, the higher ionic charge and consequent larger cubic separation 20,000 cm^{-1} and much smaller positive spin-orbit coupling gives much smaller negative orbital contribution (about 5%) to the moment.

We shall next consider the anisotropy of the Cu^{2+} ion It will be seen from the Table I that at 300°K the ionic anisotropy and mean susceptibility data for the tetrahedral Cu^{2+} are :

$$K_{\parallel} - K_{\perp} = 526 \times 10^{-6}$$

$$K = 1680 \times 10^{-6}$$

which show that the anisotropy of the ion is quite high, i.e. 526/1680, nearly 30 percent. The ionic anisotropy and mean susceptibility of octahedrally co-ordinated Fe^{2+} ion in the salt $Fe(NH_4SO_4)_2 \cdot 6H_2O$ at 300°K (Bose, 1948) are :

$$K_{\parallel} - K_{\perp} = 4229 \times 10^{-6}$$

$$K = 12698 \times 10^{-6}$$

which indicate that the octahedral Fe^{2+} ion also shows a high anisotropy i.e. nearly 33 percent. Thus we observe that the anisotropies of tetrahedral Cu^{2+} and octahedral Fe^{2+} are of the same order. As we remarked at the beginning, all the considerations in the two cases are not identical. For example, as we have seen earlier, the spin-orbit coupling is nearly eight times in Cu^{2+}, the mean magnetic moment is roughly three times less and anisotropic field itself is very large in Cu^{2+}. So that the magnetic anisotropy should have been much more in tetrahedral Cu^{2+}. Even between the octahedral and tetrahedral Cu^{2+} where both these factors are the same, the latter should have a much larger anisotropy because of the inversion of the doublet and triplet. But this is not found to be the case.

So it appears that the anisotropic behaviours here are more complicated than can be explained by a simple inversion of the levels and has to be considered against the background of complicated theoretical expressions involving a number of contributing factors.

(ii) *Variation of Ionic Moments with Temperature*

From the figure (2), we observe that the ionic moment perpendicular to the tetragonal axis shows a smaller temperature dependence and the curve ($K_\perp \cdot T$) is almost a straight line with small slope to the temperature axis, whereas the ionic moment along the parallel direction shows a much larger temperature dependence with a small curvature. This is reasonable since the orbital moment along the

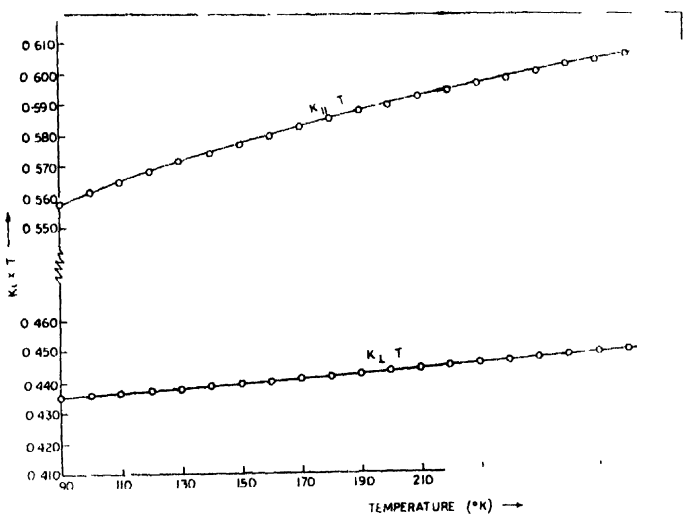

Fig. 2. The Variation of $K_\perp T$ with Temperature in $CuCs_2Cl_4$

perpendicular direction is quenched to a much larger extent than along the parallel direction, the actual values of changes of ionic moments in our temperature range being 9 and 3 percents respectively. The corresponding changes in ionic moments along and perpendicular to the tetragonal axis in octahdral Fe^{2+} ion (Bose. 1948) are 43 and 20 percents respectively. Thus we observe that the variations in the ionic moments in $CuCs_2Cl_4$ ion are very small in comparison to the octahedral Fe^{2+} ion. In octahedral Cu^{2+} ion the temperature variation of the moment is also very small. These facts are consistent with the spectral findings that in $Cu_2Cs_2Cl_4$ an orbital singlet lies lowest, with a large separation with the next highr level.

(iii) *Variation of 'Anisotropic Moment'* ($\Delta k \cdot T$) *with Temberature* :

The plot of $(K_\parallel - K_\perp)$. T against T (Fig. 3) for $CuCs_2Cl_4$ shows that the $(K_\parallel - K_\perp)$. T decreases with temperature with a large curvature. The change in the values of $\Delta k \cdot T$ between 300°K and 90°K is nearly 23 percent. A similar

plot for octahedral Cu^{2+}, say in $Cu(KSO_4)_2$. $6H_2O$ (Bose *et al*, 1957) shows that the curve has a small slope to the temperature axis and with smaller curvature.

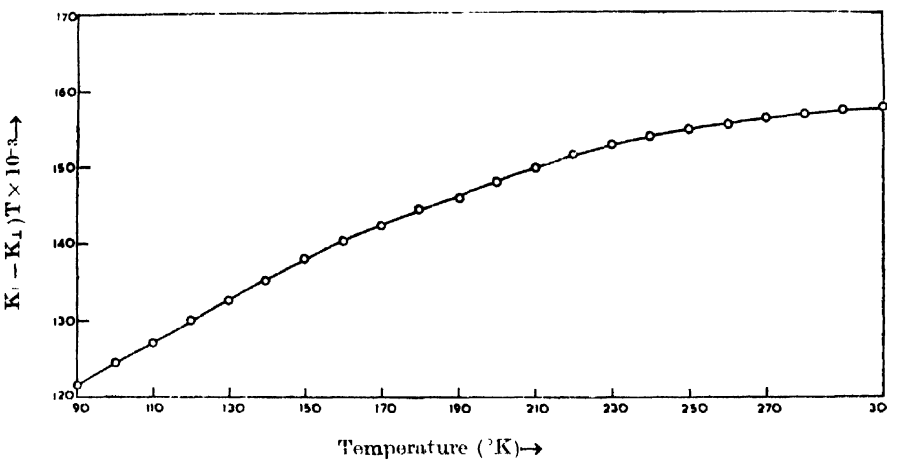

Fig. 3. Variation of $(K_{\parallel}-K_{\perp})$. T with Temperature in $CuCs_2Cl_4$

In the case of $Cu(NH_4SO_4)_2 \cdot 6H_2O$ such curvature is very large and anomalous. The variation of $\Delta k \cdot T$ in the same temperature range is nearly 9 percent. It is thus clear that the thermal behaviour of the anisotropic moment in this as in in the $Cu(NH_4SO_4)_2 \cdot 6H_2O$ is inconsistent with a theory in which the field and other parameters are constants with temperature.

(iv) *Fitting of the Mean Susceptibility and Anisotropy Data with Detailed Theory* :

The results of the fitting of the experimental data by the trial and error method already described in detailed, with the expressions of ionic susceptibilities are given in Table IV. From the Table IV we find that in order to fit the experimental data between our temperature range, the orbital factors are reduced anisotropically to $\kappa_{\parallel} = .81$ and $\kappa_{\perp} = .72$ and the spin-orbit coupling coefficient along and perpendicular to the tetragonal axis is reduced by 27 and 30 percents respectively from its free ion value of $-829\ cm^{-1}$. Thus it indicates a large anisotropic covalency overlap between the $3d$ orbital of the Cu^{2+} ion and the s- and p-orbitals of the ligand chlorines. The values of the second and fourth order tetragonal field parameters, H and I, have been chosen consistently with the other field parameters as $H = 300\ cm^{-1}$ and $I = 240\ cm^{-1}$. It is also observed that the fitting of the mean susceptibility data at all temperatures is fairly close, though a small systematic departure of about 0.5% above experimental errors ($\pm 0.2\%$) is observed at higher temperatures. A good fit might have been obtained with the mean susceptibility at all temperatures by adjusting the parameters slightly. But in view of what follows, this matters very little. The fitting of the anisotropy data at 90°K is well within experimental errors, as it should be, but systematic

TABLE IV

$G = 900\ cm^{-1}$	$\kappa_{\|} = 0.81$	$R_{\|} = 0.73$
$H = 300\ cm^{-1}$	$\kappa_{\perp} = 0.72$	$R_{\perp} = 0.70$
$I = 240\ cm^{-1}$	$\zeta = -829\ cm^{-1}$ (free ion value)	

(1) Spectroscopic energy levels

	Theoretical	Experimental (at 77°K)
E_2-E_1	5100 cm^{-1}	5000 cm^{-1}
E_3-E_1	8100 cm^{-1}	7900 cm^{-1}
E_4-E_1	9300 cm^{-1}	9050 cm^{-1}

(2) g-values :

	Theoretical	Experimental (at 77°K)
$G_{\|} =$	2.410	$G_1 = 2.384 \pm 0.006$
$G_{\perp} =$	2.141	$G_2 = 2.083 \pm 0.001$
		$G_3 = 2.105 \pm 0.006$

(3) Magnetic Susceptibility and Anisotropy

Temperature	Experimental		Theoretical	
	$K \times 10^6$	$(K_{\|} - K_{\perp}) \times 10^6$	$K \times 10^6$	$(K_{\|} - K_{\perp}) \times 10^6$
300	1680	526	1660	495
250	1973	618	1898	572
200	2420	734	2441	689
150	3231	934	3222	882
90	5321	1350	5352	1347

large departures are observed as the temperature increases, so that at 300°K or near the disagreement between the calculated and experimental values is about 7 percent. Attempts to adjust the parameters to reduce this departure in anisotropy caused an increased misfit in mean susceptibility. Elaborate trial and error calculations show that no single set of parameters could fit all values of both anisotropies and mean susceptibilities at all temperatures and also remain consistent with optical and paramagnetic resonance data. The fitting shown in the Table IV is the closest, with the set of parameters given in round numbers. The reason of this discrepancy is as follows. We have assumed all the parameters to remain constant with temperature. But there are experimental findings to suggest

that at least the anisotropic field parameters do vary with temperature, often considerably (Bose *et al*, 1960, 1961a, 1961b, 1964). The large deviation of our anisotropy curve mentioned above indicates the same. A consideration of the variation of the above field parameters may lead to a better fitting of the susceptibility and anisotropy data at all temperatures, but then if both H and I, the independent anisoptropic field parameters are assumed to change with temperature, our set of mean susceptibility and anisotropy data would not be enough to give unique solution of their values at different temperatures. Relative values of $\kappa_{\|}$, $\kappa_{\perp}$ and $R_{\|}$, $R_{\perp}$ are dependent on H and I though not explicitly and need not be considered as varying independently. For this purpose more detailed data on optical absorption or paramagnetic resonance at different temperatures would be necessary In our present calculations since we would not consider such variations in H and I, it is to be expected that the fixed set of parameters used should not be able to give a unique fitting with the mean susceptibilities and anisotropies at all temperatures, consistent with the optical fine structure and resonance data. The very perceptible discrepancy in the fitting of the magnetic anisotropy can be then ascribed to a large extent to the temperature dependence of the parameters H and I and the concommunitant dependance of $\kappa_{\|}$, $\kappa_{\perp}$, $R_{\|}$, $R_{\perp}$. There is another point to be considered. While calculating the ionic anisotropies at different temperatures, we have used the direction cosines and assumed it to be constant with temperature because in calculating $(K_{\|}-K_{\perp})$ we have used only the direction cosine of $K_{\|}$ against b axis, $\beta = 0$, which is not likely to change because of the peculiarity of symmetry requirement in the arrangement of the Cu^{2+} ions in the unit cell. This may not be quite correct and present deviation between the calculated and experimental anisotropy data may be partly due to this neglet In any case, such a variation of the direction cosine with the temperature may be inherently connected with changes in the anisotropic coefficients since that would change the packing in the unit cell and cause an induced distortion in the primary Jahn-Teller Cluster $(CuCl_4)^{2-}$ (Van Vlec, 1939) Since the direction cosines and field parameters appear independently, it is not possible in the absence of low temperature X-ray data to calculate the effect of these changes of one upon the other. The apparent changes in the anisotropic fields are obviously brought about by anisotropic thermal expansion of the lattice which would not only change orientations and distances of the ligand charges but also changes the direction cosines referred to. Moreover, the spin-lattice relaxation process acting through the ligand fields, and responsible for keeping the equilibrium of the spin orientation energy with the lattice vibrational and rotational energy may change considerably with temperature and might cause an appreciable change in Jahn-Teller anisotropy effect. It has been assumed here that the cubic field and the convalency overlap are independent of temperature. Though this is not stringtly correct, the effects of these are perhaps very much smaller than the effect of thermal changes of the anisotropic field upon the magnetic anisotropy.

(v) *Fitting of the Paramagnetic Resonance Data* :

The paramagnetic resonance study of this crystal has been done very recently by Sharnoff (1964). Measurements were carried out at 77 $^{\circ}K$. Though the unit cell of this crystal contains two pairs of magnetically inequivalent ions, the p.m.r. spectrum consists of a single line for all orientations of the crystal in the external magnetic field. The presence of one line in the p.m.r. spectrum has been ascribed to the exchange interaction which couples the spins of the paramagnetic ions. In order to confirm this and to obtain correct principal ionic g_i-values, he studied $CuCs_2Cl_4$ diluted with isomorphous $ZnCs_2Cl_4$ and obtained two lines.

The experimental principal ionic g-values at 77°K and theoretical values calculated with our choice of parameters at 90°K are given below for comparison

Calculated	Experimental
$G_{\parallel} = 2.410$	G_1 2.38 ± .006
$G_{\perp} = 2.141$	G_2 2.08 ± .006
	G_3 2.105 ± .006

The p.m.r. spectrum indicates that the $(CuCl_4)^{2-}$ cluster is really orthorhombic though as is apparent from the above values G_2 and G_3, the departure from tetragonality is rather small so as to justify our tetragonal approximation. It is also evident that the mean of G_2 and G_3 about 2.093 is somewhat different from our $G_{\perp} = 2.141$ and $G_{\parallel} = 2.41$ from $G_1 = 2.38$. These are to be expected since (1) the temperatures of measurements for the two sets are somewhat different, (2) the mixed salt used to get proper resolution of p.m.r. spectra though isomorphous with the pure salt should have appreciably different anisotropic ligand fields (3) and for the reason noted in previous section namely that our choice set of the parameters is to some extent dependent on the errors in spectroscopic fine structure data, until full consideration of their temperature variation has been allowed for (4) the direction cosine data used in magnetic results was calculated for room temperature. However, the fairly close agreement serves as a check for our result and limiting the labour in the trial and error calculation, by giving at once the orders of magnitudes of the parameters to start with.

(iv) *Fitting of the Fine structure Optical Absorption Data* :

As has been already discussed though the above choice of parameters H and I near 90°K is not compatible with magnetic data at all temperatures, these are quite consistent with the fine structure optical absorption data of Ferrguson (1964) at low temperature. The table IV shows that the agreement between the calculated and observed values of the energy levels are not quite perfect. This may be just owing to rounding off of the values of H and I in magnetic calculations. It is also to be noted that a small actual difference may exist between the separations of the levels at the temperature of observation 77°K and at our temperature of magnetic fitting 90°K.

(b) Ni^{2+}

(i) *Mean Moment and Its Variation with Temperature* :

As we have remarked earlier the magnetic behaviour of tetrahedrally co-ordinated Ni^{2+} salts should be somewhat similar to the octahedrally co-ordinated Co^{2+} salts, showing a high anisotropy, high orbital contribution to the magnetic moment and large deviation from Curie law. Unfortunately the present crystal being of cubic class, we could not study the magnetic anisotropy directly. However a scrutiny of its mean moment may provide some information in this respect through the higher order terms involving the anisotropic splittings. The effective mean moment (p_f) of this ion in $[(C_2H_5)_4N]_2[NiBr_4]$ at 300°K is 3.79 as against 3.17 of octahedrally co-ordinated Ni^{2+} ion in $Ni(KSO_4)_2 \cdot 6H_2O$ (Bose, 1948) . The spin only value for the ^3F ground state of Ni^{2+} ion is 2 83. The p_f value for octahedrally co-ordinated Co^{2+} ion in $CoSiF_6 \cdot 6H_2O$ at 300°K is 5.01 (Majumdar *et al*, 1965), the spin only value being 3.87. Thus the tetrahedral Ni^{2+} ion shows nearly 34% orbital contribution compared to about 32% for octahedral Co^{2+} and about 12% for octahedral Ni^{2+}, as is to be expected. In Ni^{2+} the higher value of spin orbit coupling compared to Co^{2+} is no doubt responsible for a large orbital contribution, even if the energy level separation had been the same which is surely not the case since D_q is 4/9 times less in magnitude.

Again the variation of experimental p_f^2 value of the tetrahedral Ni^{2+} with temperature (Fig. 4) shows a large deviation from the Curie law similar to octahedral Co^{2+} ion but unlike the octahedral Ni^{2+} ion in which the magnetic moment roughly obeys a Curie law. The experimental p_f^2-curve (Fig. 4) shows that the

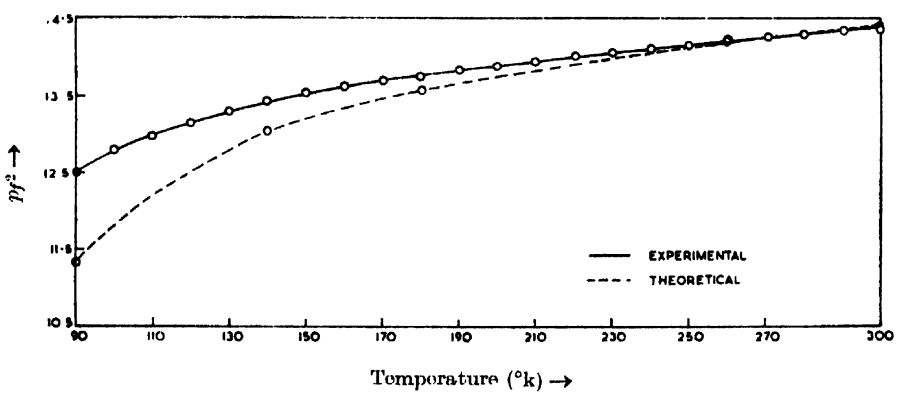

Fig. 4. Variation of p_f^2 with temperature in $[(C_2H_5)_4N]_2NiBr_4$.

p_f^2 value first gradually decreases with a slope to the temperature axis and then after about 200°K the graph has an increasing curvature.

It is seen from the Stark pattern of the tetrahedral Ni^{2+} ion (Fig. 1b; see Bose *et al*, 1965b) that after the spin-orbit coupling, a singlet ϕ_0 lies lowest. Just

above that is a doublet (ϕ_1, ϕ'_2) at about 140 cm^{-1} and the next higher level ϕ_2 (singlet) lies much higher, at nearly 1000 cm^{-1}. ϕ_0 is a non-magnetic level and so its own contribution to the magnetic moment is zero. The contribution of (ϕ_1, ϕ_1') is proportional to $e^{D/kT}$ where D is the energy separation of this level from the ϕ_0. The next higher level (ϕ_2) is too high above to be populated at ordinary temperatures, and the contribution of such level will be of the high frequency type only. When the temperature decreases, the upper doublet (ϕ_1, ϕ'_1) will gradually be depopulated and a steady fall in magnetic moment will result so long as $D < kT$. When $D \approx kT$ the rate of decrease will be faster and for any further lowering of temperature ($D > kT$, i.e. below $\sim$ 200°K) a steep fall in magnetic moment tending to zero except for high frequency contributions will result. This is very beautifully illustrated in the case of octahedral V^{3+} ion which has qualitatively the same ligand field pattern except as modified by the facts that the values of D is only $\sim$ 8 cm^{-1} and ζ - 106 cm^{-1}, with a very steep fall in the p_f^2--T curve below 10°K (Soigert and Vandon Handel, 1937; Chakravarty, 1959). In the present case, however, the experimental curve does not show such a steep fall, of magnetic moment in our temperature range for mainly two reason. The first is that the range of temperature between 200°K to 0°K is sufficient to cause a more gradual fall and the high frequency contributions are of more importance. The other more interesting reason is that the anisotropic field may change with temperature in such a way as to counteract the rate of decrease of the moment. This will be discussed in details below.

(ii) *Fitting of the mean susceptibility data with the Detailed Theory* :

By fitting the experimental data with the expression of susceptibility given in equation (8) as discussed earlier, we find (Table V) that the set of values of the parameters so obtained are : $P_{\|} = -240\ cm^{-1}$, $P_{\perp} = -375\ cm^{-1}$ $Q_{\|} = 0.7$, $Q_{\perp} = 1.024$ and $\Delta = -1020\ cm^{-1}$. Under the present circumstances, we are not

TABLE V

$P_{\|} = -240\ cm^{-1}$ $\quad Q_{\|} = 0.700$

$P_{\perp} = -375\ cm^{-1}$ $\quad Q_{\perp} = 1.624$

$\Delta = -1029\ cm^{-1}$

Temperature °K	Experimental		Theoretical		Deviations
	$\bar{K} \times 10^6$	p_f^2	$\bar{K} \times 10^6$	p_f^2	in K
300	5986	14.36	6008	14.41	− 22
260	6840	14.22	6840	14.22	0
180	9536	14.72	9421	13.56	+ 115
140	11909	13 33	11643	13.03	+ 266
90	17358	12.49	15732	11.32	+ 1626

able to separately calculate α_i's, k_i's, ζ_i's from P's and Q's. $P_{||}$ and $P_{\perp}$ can then be further written as $P_{||} = \alpha R_{||}\zeta$ and $P_{\perp} = \alpha' R_{\perp}\zeta$ where $\zeta(= -325\ \text{cm}^{-1})$ is the free ion value and so $\alpha R_{||} = 0.74$ and $\alpha' R_{\perp} = 1.15$. $R_i(||$ or $\perp)$ is the reduction factor associated with the matrix elements for spin-orbit coupling. These reductions are due to the anisotropic overlap of the surrounding s-and p-charge clouds and the admixture of $3d^74p$ and $3d^8$ configuration. α, α' are the effective Lande' splitting factors in the crystal and are different from the value 3/2 for the case of an isotropic field.

From the Table V we find that at 300°K and at 260°K the agreement between the experimental and theoretically calculated values is well within the experimental errors. But at lower temperatures, this difference increases beyond experimental error, e.g., at 180°K it is 1.2%, at 140°K ~ 3.0% and at 90°K ~ 9%. This shows that there is a systematic increase in the difference between the experimental and theoretically calculated values. In the p_f^2-T plot, the theoretical curve as we have discussed earlier shows a steeper fall after 200°K than the experimental curve. This discrepancy is evidently only due to the fact that we have assumed Δ, the anisotropy field coefficient as constant with temperature, the other factors controlling the curvature mentioned before namely the range of temperature through which the population of the level (ϕ_1, ϕ'_1) is drained into the lowest state ϕ_0 and high frequency contribution being already taken into account in the theory. From what we have discussed earlier, this variation of Δ with temperature is just as much as is required to wipe out this discrepancy at the different temperatures and evidently must be occurring in this salt as in the other cases. Of course, as Δ changes, the relative values of $P_{||}$, $P_{\perp}$ and $Q_{||}$, $Q_{\perp}$ also change with temperature, thus sharing the task of wiping out the discrepancy and keeping the apparent variation of Δ to reasonable magnitudes. This is particularly true for the tetrahedral complexes in which the anisotropic field admixtures and overlaps are comparatively larger than in the octahedral complexes and temperature variation of Δ may have greater influence on $(P_{||}, P_{\perp})$ and $(Q_{||}, Q_{\perp})$ than in the later case, however, as we have discussed earlier, we could not calculate the actual temperature vatiations of the parameters because then we could not decide the values of the parameters uniquely with the help of optical absorption and means susceptibility data alone, which are rather insensitive to the variations of the anisotropic field with temperature. So we have to remain satisfied by giving only the systematic deviation between the experimental and theoretical values.

(c) Co^{2+}

(i) *Room Temperature Mean Moment and Anisotropy* :

As we have seen earlier, the magnetic behaviours of the tetrahedrally coordinated Co^{+2} should be similar to octahedral Ni^{2+}. The effective mean moment of tetrahedral Co^{2+} ion is 300°K in $CoCs_3Cl_5$ is 4.67, the spin only value being 3.87, so that the orbital contribution is about 20 percent. This contribution

in the case of octahedral Co^{2+} and Ni^{2+} have been already calculated to be about 30 and 12 percents respectively. Thus we observe that the orbital contribution in tetrahedral Co^{2+} lies in between octahedral Ni^{2+} and Co^{2+}. It is to be remembered that the spin-orbit coupling in Co^{2+} is less than half of Ni^{2+} so that orbital contribution in the former should have been smaller. But on the other hand, the cubic field separation in the tetrahedral Co^{2+} is less than half of octahedral Ni^{2+} which obviously more than makes up the deficiency. This very likely arises from the appreciable difference in the contributions from the higher order terms in equation (9) and is also from differences in the anisotropic field constants, covalency factors and spin orbit coupling reductions in the two cases.

Again the magnetic anisotropy and mean susceptibility of tetrahedral Co^{2+} ion (Table III) at 300°K are

$$K_{\parallel} = K_{\perp} = 652 \times 10^{-6}$$

$$K = 9093 \times 10^{-6}$$

The above data show that the anisotropy is small, only about 7 percent. The magnetic data for octahedral Co^{2+} ion in $Co(KSO_4)_2.6H_2O$ at 300°K (Bose, 1948) are

$$K_{\parallel} = K_{\perp} = 3090 \times 10^{-5}$$

$$K = 10514 \times 10^{-6}$$

showing an anisotropy of nearly 30 percent. But the corresponding values for octahedral Ni^{2+} in $Ni(KSO_4)_2.6H_2O$ at 300°K (Bose *et al*, 1958) are

$$K_{\parallel} - K_{\perp} = 262 \times 10^{-6}$$

$$K = 4393 \times 10^{-6}$$

so that the anisotropy is only about 6 percent. All these facts are in accord with the theory of Van Vleck (1932).

After this work was completed and while this detailed report of the work was being prepared, Figgis *et al* (June, 1964) published a paper on the magnetic measurements of this crystal. A preliminary report of our work was, however, already sent by us in February 1964 for reading at the International conference on Magnetism, held at Nottingham. It would be seen that the mean susceptibility data of Figgis *et al* (1964) and that of ours are in good agreement but the anisotropy data at room temperature differs nearly by 6 percent The reason of this difference may be due to three factors.

(a) They have measured the anisotropy taking $K_3Fe(CN)_6$ as secondary and have taken its room temperature anisotropy values from Guha (1950) who had taken the standard room temperature data from the earlier works of Krishnan *et al* (1936) when the anisotropy method was yet to be well standardised. It has been actually shown by Stout and Griefel (1950) and Datta (1954) by more

accurate measurements that the values obtained by them in many cases differed widely from the earlier measurements of Krishnan *et al* (1934, 1936) and hence the high values obtained by Figgis *et al* (1964) may be due to this reason. It can be mentioned that our anisotropy data agrees well with Krishnan *et al* (1938) when their method was much improved.

(b) Figgis *et al* (1964) have adopted the old critical couple method, which is in many ways inferior to our present null method particularly for low anisotropies shown by Dutta-Roy (1958) and has been already discussed at length.

(c) Anisotropies of shape and diamagnetism have not been corrected for by Figgis *et al* (1964) which may be important for crystals with low magnetic anisotropy.

(ii) *Variation of Ionic Moments and Ionic Anisotropy Moment with Tempera-* : ture :

The ionic moments ($K_i \cdot T$) parallel and perpendicular to the tetragonal axis have been plotted against temperature in Fig. 5. The temperature variations

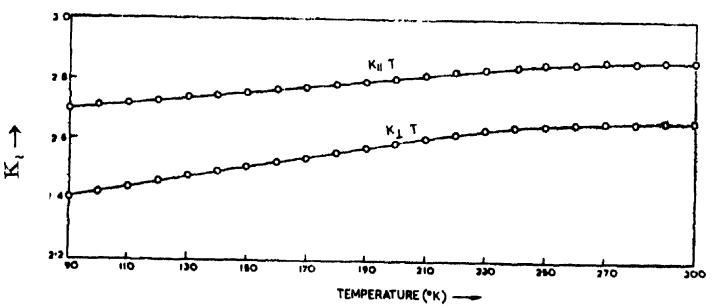

Fig. 5. Variation of $K_i.T$ with Temperature in $CoCS_3CL_5$.

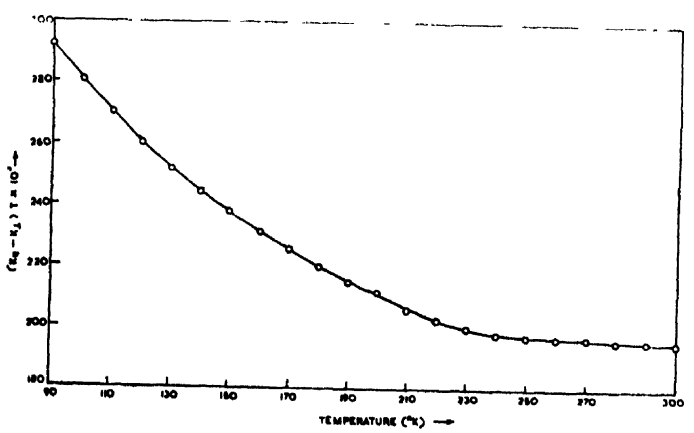

Fig. 6. Variation of $(K_{\parallel} - K_{\perp})$. with temperature in $CoCs_3Cl_5$

of ionic momonts for both the directions are nearly similar and obey the Curie-Weiss law with small different values of Weiss constant The ionic moments of octahedrally co-ordinatelyNi^{2+} salts also show similar behavious.

The curve of $(K_{\|}-K_{\perp})$. T against (Fig. 6) shows that the values of $(\Delta K.T)$ increases with temperature, as in octahedrally co-ordinated Ni^{2+} ion, though the increment in the latter case is less than in the former. This value in the case of octahedral Co^{2+} ion also increases with temperatures.

(iii) *Fitting of the Mean Susceptibility and Anisotropy Data with the Detailed theory* :

The results of the fitting of the experimental data with the expressions of ionic susceptibilities are given in Table VI. From the table we find that in order

TABLE VI

$D_q = 325\ cm^{-1}$ $\zeta_{\|} = -148\ cm^{-1}$ $k_{\|} = 0.920$
$H = 173\ cm^{-1}$ $\zeta_{\perp} = -153\ cm^{-1}$ $k_{\perp} = 0.906$
$I = -26\ cm^{-1}$

(1) Paramagnetic Resonance Data

	Experimental (at 90°K)	Theoretical
$g_{\|}$	2.32 ± 0.04	$g_{\|} = 2.377$
$g_{\perp}$	2.27 ± 0.04	$g_{\perp} = 2.324$
2D	$= -9.0\ cm^{-1}$	$2D = -6.0\ cm^{-1}$

(2) Magnetic Susceptibility and Anisotropy data :

Temperature °K	Experimental $K \times 10^6$	Experimental $(K_{\|} - K_{\perp}) \times 10^6$	Theoretical $\bar{K} \times 10$	Theoretical $(K_{\|} - K_{\perp}) \times 10^6$
300	9093	652	9106	654
250	10875	790	10872	799
200	13300	1073	13396	1037
150	17264	1581	17676	1496
90	27807	3248	29115	3084

to fit the experimental data between our temperature range, the orbital reduction factors have to be taken as $\kappa_{\|} = 0.920$ and $\kappa_{\perp} = 0.906$ and the spin-orbit coupling coefficient as $\zeta_{\|} = -148\ cm^{-1}$ and $\zeta_{\perp} = -153\ cm^{-1}$, the free ion value being $-180\ cm^{-1}$. These reductions indicate an appreciable anisotropic convalency overlap between the $3d$ orbitals of Co^{2+} ion and the s- and p-orbitals of the ligand chlories. The values of the second and fourth order tetragonal field parameters, H and I have been chosen, consistent with spectroscopic data, as $H = 173\ cm^{-1}$

and I $-26\,cm^{-1}$. It is observed that the fitting of both the anisotropy and mean susceptibility data is within the experimental errors at 300°K, but increased differences between the experimental and theoretically calculated values are observed at lower temperatures, so much so that at 90°K, this difference is about 5 percent, and much beyond the limit of experimental errors. The reason of this discrepancy is as follows. We have assumed all the parameters to remain constant with temperature. But there are adequate experimental findings to show that at least the anisotropic field parameters do vary with temperature, often considerably (Bose *et al*, 1960 1961a, 1961b, 1964). A consideration of the variation of the above field parameters may lead to a better fitting of the mean susceptibility and anisotropy at all temperatures. If H and I, the independent anisotropic field parameters, are assumed to vary with temperature, our set of mean susceptibility and anisotropy data would be just enough to give a unique solution of their values at other temperatures, consistant with the room temperature values of parameters fitting the spectroscopic data. But then it would not be possible to vary $k_{\|}$, $k_{\perp}$ and $\zeta_{\|}$ $\zeta_{\perp}$ which though dependent on H and I are not explicitly related to them. It is then evident that the room temperature parameters though uniquely determined from magnetic and spectroscopic data can not fit at low temperatures. We could have exactly fitted the entire range of values of susceptibility and anisotropy with a hypothetical fixed set of parameters using only the magnetic measurements since we have enough magnetic data for this purpose, but his set of parameters would not be consistent with spectroscopic or resonance data. In our present calculation since we could not consider such variation in H and I as well as $k_{\|}$, $k_{\perp}$, $\zeta_{\|}$, $\zeta_{\perp}$ in the absence of temperature variation data on spectroscopic absorption and paramagnetic resonance, we had to remain satisfied by showing that the fixed set of parameters consistent with spectroscopic absorption data at room temperature could not give unique fitting with the experimental data at all temperatures. This is further brought out by the fact that the zero-field splitting (-6 cm ^{1}) calculated uniquely at room temperature is appreciably different from the experimental value -9 cm ^{1} at low temperature. The very perceptible and consistently increasing discrepancy in the fitting of anisotropy and mean susceptibility at other temperatures can then be ascribed to a large extent to the temperature dependence of the parameters H and I and concommitant dependence of $k_{\|}$, $k_{\perp}$, $\zeta_{\|}$, $\zeta_{\perp}$. Evidently the fixed set of parameters at all temperatures and a zero-field splitting as large as $-20\,cm^{-1}$ postulated by Figgis *et al* (1964) is against all experimental facts even if the large errors in their anisotropy values is overlooked. They have further postulated a weak super exchange interaction (J $\sim 0.5\,cm^{-1}$) between Co^{2+} ions through the nearest intermediaty chlorines to close up the still existing discrepancy with the theory. It is of course possible that such a small exchange interaction exists though p.m.r. (Hall and Hayes, 1960) and Zeeman field splitting studies (Judd, 1964) do not report any. But even taking into account this interaction, causing a small departure from Curie Law, the whole

from this law can not be covered unless a very unlikely observed departure value of zero-field splitting is taken as done by Figgis *et al* (1964) on an adhoc basis.

(iv) *Fitting of the Paramagnetic Resonance Data* :

Paramagnetic resonance measurements on the single cyrstals of $CoCs_3Cl_5$ were done by Bowers and Own (1955) and by Hall and Hyes (1960) at 90 K The set of the theoretical parameters which gives good fit with the susceptibility and anisotropy data at room temperature was utilised to calculated the 'g' and 'D' values. The experimental and theoretical values are given below :

Experimental	Theoretical
$g_{\parallel} = 2.32 \pm 0.04$	$g_{\parallel} = 2.377$
$g_{\perp} = 2.28 \pm 0.04$	$g_{\perp} = 2.325$
$2D = -9.0\ cm^{-1}$	$2D = -6.0\ cm^{-1}$

It would be seen that there is a small but appreciable difference between the experimental and theoretical values particularly the D value. This difference between them is due to the fact that we have calculated the g_i and D with the help of parameters which give good fit with the mean susceptibility and anisotropy data only at room temperature. Hence the ezlculated g_i and $2D$ values refer to the values at room temperature whereas the experimental values are for 90K. This shows a variation of the 'g' and $2D$ values in this temperature region indicating a change in the crystal field as we had anticipated earlier. It is to be noted that Figgis *et al*'s value for $2D$ is $-20\ cm^{-1}$ which does not agree in magnitude with the resonance values.

(v) *Fitting of the Optical Absorption Data* .

As had already been discussed, although the above choice of parameters derived from susceptibility and anisotropy data, is not compatible with the magnetic data at all temperatures, these are quite consistent with the fine structure optical absorption data at room temperature. Considering cubic and tetragonal fields and spin-orbit coupling, the main bands ν_2 and ν_3 break into six components which are in good agreement with the experimental fine structure levels (Cotton *et al*, 1961).

AN APPARENT DISCREPANCY BETWEEN STRUCTURAL ANALYSIS AND MAGNETIC MEASUREMENTS IN $CuCs_2Cl_4$

As we have seen earlier, the structural analysis of $CuCs_2Cl_4$ by Helmohlz and Kruh (1952) reveals that the tetrahedron of four chlorine atoms is compressed along the tetragonal axis and the other two perpendicular axes are equal. Hence the field along this direction might have been considered to be stronger than along the former would have been quenched to a greater extent than in the perpendicular

direction; consequently $K_\perp$ would appear to be greater than $K_\parallel$. But we experimentally observe that $K_\parallel$ is greater than $K_\perp$. This is supported by the spectroscopic studies (Ferguson, 1964) showing that the singlet $^2B_2$ is below the doublet $^2E_2$ as is to be expected in this case and also directly by the e.s.r. studies of Sharnoff (1964) giving $G_\parallel > G_\perp$ A similar results has been obtained recently in $FeSiF_6{\cdot}6H_vO$ (trigonal crystal, space group C^2_{3i} with one molecule in the unit cell) where neutron diffraction studies (Hamilton, 1961) indicate the $(Fe(6H_2O)]^{2+}$ octahedron to be elongated, whereas magnetic measurements of Jackson (1959) and Bose and Rai (1965) uniquely show that $K_\perp > K_\parallel$.

A qualitative explanation of the present discrepancy was given by Mitra (1964) who tried to account for this on the basis of anisotropic covalency overlap of the orbitals of the ligands and the metal ion, which in consequence may cause an anisotropic reduction of the orbital moment in a sense opposite to that of the flattering of the tetrahedron. A look at the ligand field parameters given in Table V indicates that the orbital factor K_t has been reduced anisotropically to $\kappa_\parallel = 0.81$ and $\kappa_\perp = 0.72$ along and perpendicular to the tetragonal axis, respectively, thus showing that the covalency overlap along the perpendicular direction 28 percent. The effect of covalency overlap in general is to reduce the orbital moment. Hence the reduction of the orbital moment in the perpendicular direction of th orbital moment in the perpendicular direction is nearly 9 percent more than in the parallel direction, and this in spite of the squatness of the tetrahedron may reduce the susceptibility along the perpendicular direction, so much so that it becomes smaller than the susceptibility along the parallel direction i.e. $K_\perp$ becomes less than $K_\parallel$.

REFERENCES

Bose, A., 1947, *Ind. J. Phys*, **21**, 275

Bose, A., 1948, *Ind J. Phys.*, **22**, 74, 195, 483.

Bose, A., Mitra, S. C and Datta, S. K., 1957, *Proc. Roy. Soc*, **A239**, 165.

Bose, A., Mitra, S. C. and Datta, S. K., 1958, *Proc. Roy. Soc.*, **A248**, 153.

Bose, A., Chakravarty, A. S. and Chatterji, R., 1960, *Proc. Roy. Soc.*, **A255**, 145.

Bose, A., Chakravarty, A. S. and Chatterji, R., 1961, *Proc. Roy. Soc*, **A261**, 43, 207.

Bose, A. and Chatterji, R., 1963, *Proc. Phys. Soc.*, **82**, 23.

Bose, A., Chatterji, R. and Rai, R., 1964, *Proc. Phys. Soc.*, **83**, 959

Bose, A., Dutta Roy, S. K., Ghosh, P. K. and Mitra, S., 1963, *Ind. J. Phys.*, **38**, 505.

Bose, A., Lahiri, S. and Ghosh, U. S., 1965a, *J. Phys. Chem. Solids* (In press).

Bose, R., Rai, R. and Mitra, S., 1965*b*, *Ind. J. Phys.* **39**, 318.

Bose, A., Rai, R., Kumar, S. and Mitra, S., 1965c, *Physica*, (Communicated).

Bowers, K. D., and Owen, J., 1955, *Rep. Prog. Phys.*, **18**, 304.

Cotton, F. A., Goodgame, D. M. L. and Goodgame, M., 1961, *J. Am. Chem. Soc.*, **83**, 46900.

Datta, S. K., 1954, *Ind. J. Phys.*, **28**, 239.

Dutta Roy, S. K., 1954, *Ind. J. Phys.*, **28**, 183.

Dutta Roy, S. K., 1958, D.Phil. Thesis, C.U.

Dumon J. W. M. and Cohen, E. R. 1948, *Rev. Mod. Phys.* **20**, 82.

Ferguson, J., 1964, *J. Chem. Phys.*, **40**, 3406.
Figgis, B. N., Gerloch, M. and Mason, R., 1964, *Proc. Roy. Soc.*, *A***279**, 210.
Ghosh, U. S. and Mitra, S., 1964, *Ind. J. Phys.*, **38**, 19.
Gill, N. S. and Nyholm, R. S., 1959, *J. Chem. Soc.*, 3997.
Goodgame, D. M. S. and Cotton, F. A., 1961, *J. Am. Chem. Soc.*, **83**, 4161.
Gorter, C. J., 1932, *Phys. Rev.*, **42**, 437.
Guha, B. C., 1951, *Proc. Roy. Soc.*, *A***206**, 353.
Hall, J. P. P. and Hayes, W., 1960, *J. Chem. Phys.*, **32**, 1871.
Hamilton, W. C., 1962, *Acta Cryst.*, **15**, 353.
Helmholz, L. and Kruh, R. F., 1952, *J. Am. Chem. Soc.*, **74**, 1176.
Jackson, L. C., 1959, *Phil. Mag.*, **4**, 554.
Jackson, L. C. 1297, *Phil. Trans.* **227**, 107
Jorgensen, C. K., 1956 Kgl. Danske. Videnskab Selskab. *Mat-fys. Medd.*, **29**, 11.
Judd, B. R., 1964, *Proc. Phys. Soc.*, **83**, 1036.
Krishnan, K. S. and Banerji, S., 1936, *Phil. Trans.*, *A***232**, 99.
Krishnan, K. S. and Mookherji, A., 1938, *Phil Trans.*, *A***237**, 135.
Low, W., 1960, Paramagnetic Resonance in Solids (Solid State Phys., Suppl. 2)
Mookherji, A., 1945, *Ind. J. Phys.*, **19**, 63.
Mitra, S., 1964, *Ind. J. Pure & Appl. Phys.*, **2**, 333.
Powell, H. M. and Wells, A. F., 1935, *J. Chem. Soc.*, 359.
Pryce, M. H. L., 1950, *Proc. Phys. Soc.*, *A***63**, 25.
Rai, R., and Mitra, S., 1964, *Ind. J. Phys.*, **38**, 121,
Sharnoff, M., 1961, *J. Chem. Phys.*, **41**, 2203.
Vanden, Handel, J. and Seigert, A., 1937, *Physica*, **4**, 871.
Van Vleck, J. H., 1932, *Phys. Rev.*, **41**, 208.
Van Vleck, J. H., 1939, *J. Chem. Phys.*, **7**, 61, 72.
Weakhem, H. A., 1962, *J. Chem. Phys.*, **36**, 2116.